

## APS

### **X-ray Emission Analysis of the S-state Intermediates of the Photosystem II Protein Complex**

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Large-scale implementation of manmade systems based on artificial photosynthesis to harvest solar energy could lead to abundant chemical storage of solar power in the form of hydrogen. The process of splitting water ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$ ) during photosynthesis requires a catalyst, the oxygen-evolving complex, or  $\text{Mn}_4\text{Ca}$  cluster, located within the trans-membrane metalloprotein complex photosystem II. Characterization of sub-millisecond reactive intermediates in this system is central to understanding the catalysis involved in water splitting. X-ray emission spectroscopy techniques provide information on the electronic structure of these states.

Following the progression of x-ray induced damage, we demonstrate the feasibility of collecting room-temperature Mn  $\text{K}\beta$  x-ray emission data on the dark stable S1 state of photosystem II in two different beam modes: continuous monochromatic beam and pulsed pink beam. The dosage/damage relation for continuous beam measurements matches preliminary room-temperature models well. Additionally, the determined damage thresholds, likely representative of other metalloproteins, are sufficient for the analysis of electron dynamics and the catalytic mechanism. Computational modeling of protein damage kinetics in monochromatic mode is extrapolated to higher dose deposition rates. The results support the theory of "detection before destruction" both for pulsed pink beam and free electron laser sources.

To learn more about the water-splitting step in particular, time-resolved  $\text{K}\beta$  emission laser pump (to advance the catalytic cycle), x-ray probe experiments were conducted in pulsed pink beam mode. For the first time, emission data are presented for the  $\text{S}_3 \rightarrow \text{S}_0$  transition.

Room-temperature data are shown for all S states. Analysis of the lower states agrees well with limited published results. For the water-splitting transition, we observe immediate Mn reduction, within 50  $\mu\text{s}$  from

the final flash. This result likely eliminates two of the five currently supported mechanisms of water oxidation, with radical coupling mechanisms or an  $\text{OH}^-$  nucleophilic attack left as the strong candidates.